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THERMODYNAMIC PROPERTIES OF THE LIQUID Bi-Cu-Sn LEAD-FREE SOLDER ALLOYS

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Abstract

The electromotive force measurement method was employed to determine the thermodynamic properties of liquid Bi-Cu-Sn alloys using solid electrolyte galvanic cells as shown below:

*Kanthal+**Re**, Bi-Cu-Sn, SnO_2 | **Y**ttria Stabilized **Z**irconia | air, **Pt**, $P_{O_2} = 0.21\ atm$*

Measurements were carried out for three cross-sections with constant Bi/Cu ratio equal to: 1/3, 1 and 3 and for various tin content varying every 10%, resulting in a total of 26 different alloy compositions. The temperature of the measurements varied within the range from 973 to 1325 K. A linear dependence of the e.m.f. on temperature was observed for all alloy composi-tions and the appropriate line equations were derived. Tin activities were calculated as func-tion of composition and temperature. Results were presented in tables and figures.

Keywords: Electrochemical techniques; Thermodynamic properties; Lead-free solders.

1. Introduction

Ag-Bi and Ag-Bi-Sn alloys are considered among others as possible materials for high-temperature (>230^{o}C) lead-free solders. Since copper is frequently used as substrate, it is es-sential to understand the interactions between solder and substrate, basing on the knowledge of phase equilibria in the quaternary Ag-Bi-Cu-Sn system, and Bi-Cu-Sn is one of its subter-naries.

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Thermodynamic properties of the liquid Bi-Cu-Sn alloys were determined recently by calorimetric method [1], but tin activities were not measured so far.

2.Experimental

Closed-end yttria-stabilized zirconia (YSZ) tubes (5/8 mm I/O.D. - Yamari, Japan) were used as the electrolyte and dry air (p_{O2} = 0.21atm) served as the reference electrode. Platinum wire was used for air electrode and Kanthal™ wire with rhenium tip was applied for alloy elec-trode as current leads; the cross-section through the cell is shown schematically in Fig.1.

Special cell design: Al_2O_3 tube as a shield of Kanthal wire and a pass hole in elastic cork tightened by the vacuum grease allowed moving working electrode up and down, so it was possible to open tube in lower temperature for adding definite amount of Sn to alloy to change its composition. In such a way it was possible to measure tin activities for three different alloy compositions using only one electrolyte tube. The schematic diagram of the cell assembly is presented in Fig. 2.

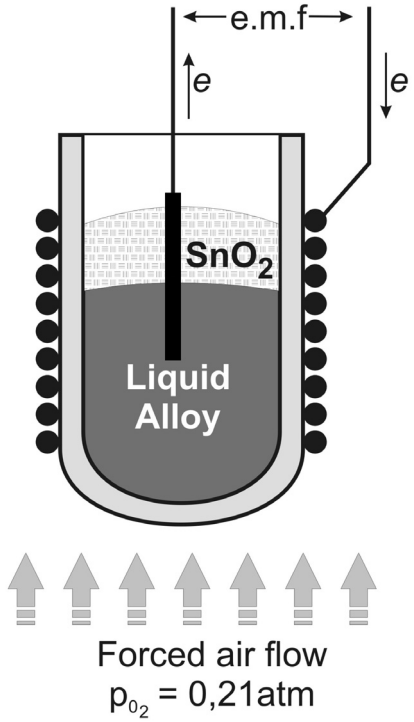

Fig. 1. Schematic cross-section of the galvanic cell.

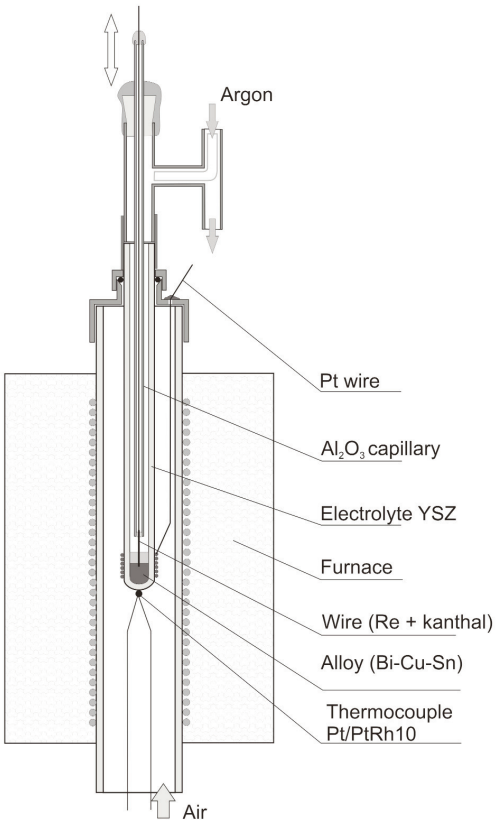

Fig. 2. Scheme of cell assembly.

Experiments were carried out in a vertical resistance furnace with the brass head, which allowed mounting the cell container within the constant temperature zone. After a constant temperature was reached, the cell

was left to stabilize electromotive force, and then the e.m.f. was recorded by data acquisition system consisted of Keithley 2000 digital voltmeter and a computer furnished with the appropriate software.

Bismuth-copper-tin alloys were prepared from pure metals (Bi and Sn 99.99%, Cu 99.999%) by direct melting in the electrolyte tube with SnO_2 (99.99%) pellet. An inert atmos-phere was maintained inside the cell by passing 5 ml/min argon gas of quality 5.0 (Linde, Poland) through the H-tube. Passing gas through the H-tube allowed a penetration by inert gas into the electrolyte tube without disturbing the local equilibrium over the sample.

The reversibility of the cell was checked by passing small current from an external source; the e.m.f. returned to the original value within ±1mV in about 1-10 min depending on the temperature. The emf readings were taken in both heating and cooling mode within the range 973-1325 K producing almost the same e.m.f. values within recorded scatter of points. The full run was completed after about 3-4 days.

3. Results and discussion

In order to determine tin activities in liquid Bi-Cu-Sn alloys the e.m.f. of the cell (I):

Kanthal+**Re**, Bi-Cu-Sn, SnO_2 | **Y**ttria Stabilized **Z**irconia | air, **Pt**, $P_{O_2} = 0.21\,atm$ (I)

was measured in the temperature range 973-1325 K and for three cross-sections with constant Bi/Cu ratio equal to: 3, 1 and 1/3 and for tin compositions varying every 10%, from 10 up to 90 at.% Sn (only in case of Bi/Cu ratio=1).

Electrode reactions are:

a) at reference electrode:

$$O_2(g) + 4e^- = 2[O^{-2}] \quad (1)$$

b) at alloy electrode:

$$Sn(l) + 2[O^{-2}] = 4e^- + SnO_2(s) \quad (2)$$

where Sn(l), e–, O_2(g) and $[O^{-2}]$ denote: tin in a liquid solution, electron, pure oxygen gas and oxygen ion, respectively.

Consequently, the overall cell (I) reaction is:

$$Sn(l) + O_2(g) = SnO_2(s) \quad (3)$$

For the reversible reaction (3) the change in Gibbs free energy can be derived as follows:

$$\Delta G(3) = -4FE = \Delta G^0_{f,SnO_2} - RT\ln a_{Sn} - RT\ln(0.21) \quad (4)$$

where:

F – Faraday's constant,

E – measured electromotive force,

$\Delta G^0_{f,SnO_2}$ - Gibbs energy of formation of tin dioxide, R – gas constant, T – absolute temperature, a_{Sn} – tin activity, 0.21 – partial pressure of oxygen in the air.

If tin is in its pure, liquid state ($X_{Sn} = 1$) equation (4) takes the form:

$$\Delta G^0_{f,SnO_2} = -4FE^0 + RT\ln(0.21) \quad (5)$$

The results of temperature dependence of e.m.f. E^O obtained for pure tin were determined in one of our previous works [2]; they can be presented in the form:

$$E^O(V) = 1.478\ (\pm 0.002) - 0.5553\ (\pm 0.0013) \cdot T \quad (6)$$

Next, by combining equations (4) and (5) the following expression for the activity of

tin in the Bi-Cu-Sn liquid alloy can be derived, as below:

$$\ln a_{Sn} = \frac{4F}{RT}(E - E^0) \quad (7)$$

All emf values were corrected for Pt-Kanthal thermoelectric power determined in the separate experiments:

Ep= -0.236363-5.45794 •

10-4T+8.31592 •10-6T^2 [mV].

Rhe-nium tip was small enough to fit the constant temperature zone, so Re-Kanthal joint did not generate of additional thermoelectric effect and the respective thermoelectric correction was not necessary.

Linear dependence of emf on temperature was observed for all alloy compositions and pa-rameters of equations:

E = a + b•T

obtained by the least square fit of emf data are listed for cross-section X_{Bi}/X_{Cu} = 3, 1 and 1/3 in Tables 1, 2 and 3, respectively, and the example of the emf versus T plot for X_{Bi}/X_{Cu} = 1 section is shown in Figure 3.

Table 1. Corrected e.m.f. versus temperature line coefficients for different tin concentration in Bi-Cu-Sn liquid alloys for cross-section X_{Bi}/X_{Cu}=3

X_{Sn}	$E = a + b \cdot T$ [V]	
	a	$b \cdot 10^3$
0.1	1.3969 ±0.0102	-0.5484 ±0.0088
0.2	1.4763 ±0.0026	-0.5968 ±0.0023
0.3	1.4735 ±0.0037	-0.5796 ±0.0033
0.4	1.4803 ±0.0049	-0.5797 ±0.0044
0.5	1.4974 ±0.0039	-0.5892 ±0.0035
0.6	1.4856 ±0.0018	-0.5729 ±0.0016
0.7	1.4901 ±0.0027	-0.5733 ±0.0024
0.8	1.4879 ±0.0043	-0.5686 ±0.0038

Table 2. Corrected e.m.f. versus temperature line coefficients for different tin concentration in Bi-Cu-Sn liquid alloys for cross-section X_{Bi}/X_{Cu}=1.

X_{Sn}	$E = a + b \cdot T$ [V]	
	a	$b \cdot 10^3$
0.1	1.4555 ±0.0033	-0.6020 ±0.0028
0.2	1.4685 ±0.0017	-0.5923 ±0.0014
0.3	1.4813 ±0.0039	-0.5911 ±0.0034
0.4	1.4859 ±0.0019	-0.5843 ±0.0017
0.5	1.4924 ±0.0021	-0.5845 ±0.0018
0.6	1.4949 ±0.0020	-0.5818 ±0.0018
0.7	1.4963 ±0.0026	-0.5785 ±0.0023
0.8	1.4925 ±0.0038	-0.5721 ±0.0034
0.9	1.4916 ±0.0037	-0.5693 ±0.0033

Table 3. Corrected e.m.f. versus temperature line coefficients for different tin concentration in Bi-Cu-Sn liquid alloys for cross-section X_{Bi}/X_{Cu}=1/3.

X_{Sn}	$E, V = a + b \cdot T$	
	a	$b \cdot 10^3$
0.1	1,4121±0,00574	-0,5788 ±0,0048
0.2	1,5100 ±0,00446	-0,6232 ±0,0038
0.3	1,4622 ±0,00732	-0,5774 ±0,0064
0.4	1,4878 ±0,00285	-0,5877 ±0,0025
0.5	1,4954 ±0,00350	-0,5866 ±0,0031
0.6	1,4916 ±0,00141	-0,5783 ±0,0012
0.7	1,4951 ±0,00268	-0,5769 ±0,0024
0.8	1,4939 ±0,00156	-0,5735 ±0,0014
0.9	1,4934 ±0,00132	-0,5711 ±0,0011

Since the statistical scatter of the emf vs T plots is very small it was assumed that emf values calculated via linear equations of Tables 1 - 3 are equal to those measured within an experi-mental error, relation (7) was used to derive activity data at two arbitrary temperatures 973 and 1273 K, and they are presented as tin activity versus tin content plots in Figures 4 – 6.

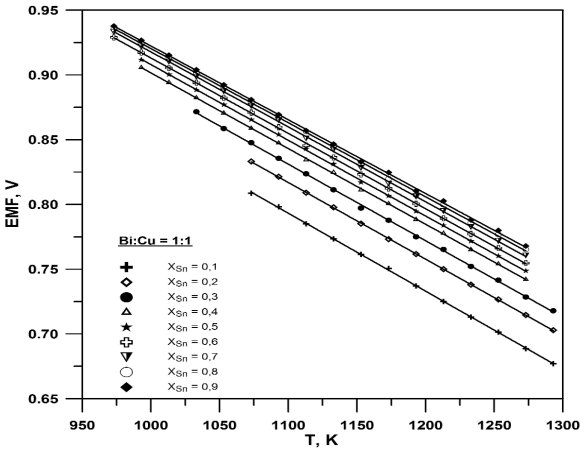

Fig. 3. E.m.f vs. temperature plots for cross-section X_{Bi}/X_{Cu}= 1.

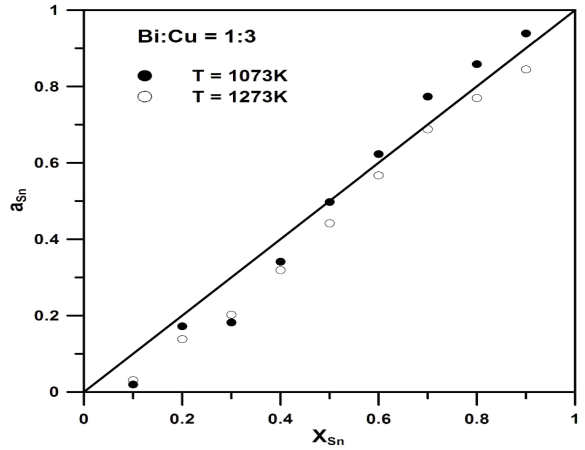

Fig. 4. Tin activity curve calculated at two temperatures for X_{Bi}/X_{Cu} = 1/3.

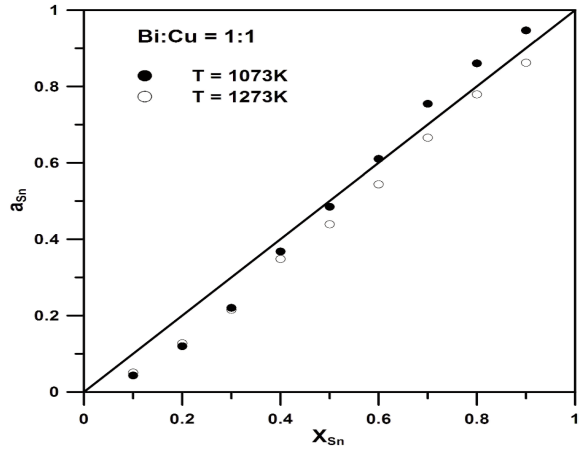

Fig. 5. Tin activity curve calculated at two temperatures for X_{Bi}/X_{Cu} = 1.

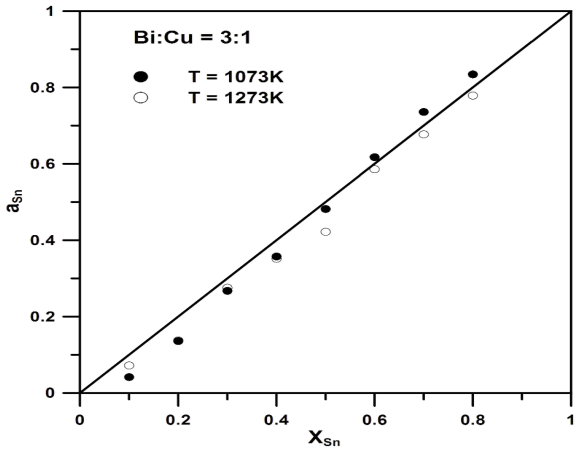

Fig. 6. Tin activity curve calculated at two temperatures for X_{Bi}/X_{Cu} = 3.

4. Conclusions

Tin activities in the liquid Bi-Cu-Sn alloys were determined for the first time by emf method using solid electrolyte galvanic cells. Linear dependence of emf on temperature was observed in all 26 compositions investigated.

Activity versus composition curves as shown in Fig. 4 - 6 display slightly negative de-viation from Raoult's rule for lower tin contents, whereas for higher ones deviation is slightly positive.

The results of this work are to be used along with calorimetric data of [1] and DTA re-sults of [3] to prepare a new thermodynamic description of Bi-Cu-Sn alloy system by CALPHAD method.

Aknowledgement

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